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(54) Process for preparing silver-based catalyst and process for epoxidising higher olefins.

(57) This invention relates to a process of oxidizing an olefin having at least three carbon atoms directly to the corresponding epoxide comprising contacting the olefin with oxygen in the presence of a catalyst comprising a mixed silver-promoter metal (+2 or +3) silicate. In the direct oxidation of propylene the process yields a high selectivity to propylene oxide. This invention also relates to a catalyst and the process for preparing said catalyst. The process comprises contacting in an aqueous solution the dissolved salts (a) a silver-containing salt; (b) at least one salt containing a multivalent cation promoter; and (c) a silicon-containing salt, wherein the mole ratio of silicon to combined silver and promoter metals is at least 0.5, under conditions sufficient to form a mixed silver-promoter silicate precipitate.

Compared to existing catalysts, the catalysts of the present invention have a higher selectivity for olefin oxides and a higher level of activity.

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PROCESS FOR PREPARING SILVER-BASED CATALYST AND PROCESS FOR EPOXIDIZING HIGHER OLEFINS

This invention relates to a catalyst and process for the direct oxidation of olefins to epoxides by molecular oxygen.

The direct oxidation of olefins to epoxides by molecular oxygen is well-known. The usual catalyst contains metallic or ionic silver, optionally modified with promoters and activators, such as alkaline earth metals or metal salts. U.S. Patent 4,007,135, for example, lists many promoters, including calcium, magnesium, strontium, cadmium, and copper. Most of the catalysts contain a porous inert support or carrier upon which the silver and promoter are deposited. A review of the direct oxidation of ethylene in the presence of such silver catalysts is given by W. M. H. Sachtler, C. Backx, and R. A. Van Santen in Catalysis Reviews: Science and Engineering, 23 (1&2), 127-149 (1981).

Some patents of the prior art teach the use of catalysts containing silver and silicon in the direct oxidation of olefins. Specifically, U.S. 3,585,217 teaches a catalyst of silver silicate, optionally containing activator compounds, for use in the epoxidation of ethylene. This catalyst is disclosed to have a low activity. U.S. 4,272,443 teaches a catalyst comprising a support coated with lithium silicates and silver salts, such as silver silicate, for the epoxidation of ethylene. Japanese Koho 1978 - 39,404 (Oda) teaches a catalyst containing predominantly elemental silver, and lesser amounts of cadmium and silicon oxides for the epoxidation of propylene.

It is well-known that most catalysts for the direct oxidation of ethylene to ethylene oxide do not give comparable results in the corresponding oxidation of the higher olefins, such as propylene. It would be desirable to have a catalyst for the direct oxidation of olefins which achieves a high selectivity for olefin oxides, particularly the higher olefin oxides. It would be even more desirable if such a catalyst were to possess a high level of activity.

The invention is the process of epoxidizing higher olefins comprising contacting at least one higher olefin with oxygen in the presence of a catalyst under conditions sufficient to produce the corresponding olefin oxide. For the purposes of this invention a higher olefin is defined as an olefin containing at least three carbon atoms. The catalyst is prepared by a process comprising contacting in an aqueous solution the following dissolved salts:

(a) a silver-containing salt;
 (b) at least one salt containing a multivalent cation promoter; and
 (c) a silicon-containing salt, wherein the mole ratio of silicon to combined silver and promoter metals is at least about 0.5,

under conditions sufficient to form a mixed silver-promoter silicate precipitate. This catalyst, when tested in the epoxidation of propylene, as described hereinafter, produces a conversion of propylene greater than 0.20 mole percent and a selectivity to propylene oxide greater than 28 mole percent.

It is surprising that the precipitation of a mixed silver-promoter silicate from a solution containing a mole ratio of silicon to combined silver and promoter metals of at least 0.5 would produce a catalyst with improved activity and selectivity in the epoxidation of the higher olefins to their corresponding olefin oxides. The epoxides formed from olefins pursuant to this invention are well-known, and are particularly useful for the production of polyether polyols.

The silver-containing salt can be any silver salt which is water-soluble and which will not adversely react with the silicate-containing salt to form an undesirable precipitate. Pertaining to the silver-containing salt, the term "water-soluble" means a solubility of at least 1.0 g silver salt per liter water. An undesirable precipitate is defined as one which interferes with the formation of the mixed silver-promoter silicate catalyst, or contaminates the mixed silver-promoter silicate catalyst. An undesirable precipitate will occur, for example, if the anion of the silver-containing salt reacts with the cation of the silicate-containing salt to yield an insoluble solid. Examples of suitable silver-containing salts include silver benzoate, silver chlorate, silver perchlorate, silver chlorite, silver fluogallate, silver fluoride, silver fluorosilicate, silver nitrate, silver nitrite, silver propionate and silver sulfate; but the silver-containing salt is not meant to be limited to only these examples. Preferred are silver chlorate, silver perchlorate, silver fluoride and silver nitrate. Most preferred is silver nitrate.

The promoter-containing salt may be any multivalent cation salt which is water-soluble and which will not adversely react with the silicate salt to form an undesirable precipitate. Pertaining to the promoter-containing salt, the term "water-soluble" means a solubility of at least 0.05 g promoter salt per liter water. An undesirable precipitate is defined hereinbefore, and may be formed if the cation of the silicate-containing salt reacts with the anion of the promoter-containing salt. Promoter-containing salts which form precipitates

with the silver-containing salt may be used, on condition that the precipitate is removed prior to addition of the silicate solution. After removal of said precipitate the amount of silver remaining in solution may have to be adjusted to replace any silver which may have been lost. Preferably, the promoter salts are water-soluble salts having dipositive or tripositive cations selected from the group consisting of Group IIA, Group VIII, 5 Group IB (excluding silver), Group IIB, and the rare earth lanthanide (atomic weights 57-71) metals. More preferably, the promoter salts are water-soluble nitrate, chlorate, perchlorate, and fluoride salts having dipositive or tripositive cations selected from the group of metals consisting of beryllium, magnesium, calcium, strontium, barium, cobalt, nickel, copper, zinc, cadmium, praseodymium, neodymium, europium, gadolinium, holmium, and lutetium. Most preferably, the promoter salts are water-soluble nitrates having 10 dipositive or tripositive cations selected from the group of metals consisting of beryllium, magnesium, calcium, strontium, barium, cobalt, nickel, copper, zinc, cadmium, praseodymium, neodymium, europium, gadolinium, holmium, and lutetium. Examples of suitable promoter salts are the following: beryllium fluoride, calcium nitrate, cadmium potassium sulfate, cobalt (II) chlorate, copper (II) nitrate, europium nitrate, nickel hypophosphate, magnesium nitrate, praseodymium (III) nitrate, and zinc borate. However, the promoter- 15 containing salts are not limited thereto.

The silicate-containing salt can be any silicate salt which is water-soluble and which will not adversely react with the silver-containing and promoter-containing salts to form an undesirable precipitate, as defined hereinbefore. More specifically, if the cation of the silicate-containing salt reacts with the anion of either the silver-containing salt or a promoter-containing salt, an undesirable precipitate may form. Pertaining to the 20 silicate-containing salt, the term "water-soluble" means a solubility of at least 1.0 g silicate salt per liter water. Examples of suitable silicate-containing salts are sodium silicate, ammonium silicate, sodium disilicate, sodium metasilicate, sodium orthosilicate, potassium metasilicate and potassium tetrasilicate; however, the silicate-containing salt is not meant to be limited thereto. Preferred are the Group IA metal silicate salts. More preferred are sodium silicate, sodium disilicate, sodium metasilicate and sodium 25 orthosilicate. It is noted that when any one of the above-identified silicate salts is dissolved in water, a distribution of silicate species is present in the solution. The distribution will depend upon the pH of the solution. Thus, for example, if an aqueous solution of sodium disilicate is prepared, the solution will contain predominately $\text{Si}_2\text{O}_5^{2-}$ anions, and lesser amounts of SiO_3^{2-} and $\text{Si}_3\text{O}_7^{2-}$ ions, plus other oligomeric species.

30 In accordance with the practice of the invention, the catalyst is prepared from an aqueous solution containing a silver-containing salt, a silicate-containing salt, and at least one salt containing a multivalent cation promoter. The mole ratio of silicon to combined silver and promoter metals may be any that gives rise to the mixed silver-promoter silicate precipitate having the catalytic properties described hereinafter. Preferably, the mole ratio of silicon to combined silver and promoter metals is at least 0.50:1. More 35 preferably, the mole ratio of silicon to combined silver and promoter metals is greater than 0.60:1, more preferably greater than about 0.70:1; preferably less than 10.0:1, more preferably less than 3.5:1. The number of moles of silicon is based on the water-soluble silicate-containing salt, and does not include the silicon arising from any silica support which may be employed. The mole ratio of silver to multivalent cation promoter may be any that gives rise to the mixed silver-promoter silicate precipitate having the catalytic 40 properties described hereinafter. Preferably, the mole ratio of silver to promoter is at least 1.0:1. More preferably, the mole ratio of silver to promoter is greater than 1.4:1, most preferably greater than 2.0:1; more preferably less than 100:1, most preferably less than 20:1. The number of moles of promoter are taken as the combined moles of all cation promoters in solution and does not include cations associated with any support which may be employed.

45 The preparation of the catalyst from the silver, promoter, and silicate-containing salts is a relatively simple procedure. Two aqueous solutions are prepared. The silicate-containing salt is mixed with sufficient water to dissolve the salt in a container, such as a glass flask or beaker, to form a first water solution. The mixing can be at room temperature and open to the atmosphere. The silver-containing salt and all of the promoter-containing salts are mixed with sufficient water to dissolve the salts in a container, such as a glass 50 flask or beaker, to form a second water solution. The mixing can also be at room temperature, or alternatively at elevated temperatures, and open to the atmosphere.

The two water solutions, described hereinabove, are contacted to form a third water solution containing the following dissolved salts: a silver-containing salt, a silicate-containing salt and at least one salt containing a promoter. The first water solution and the second water solution can be contacted in any 55 effective manner such as flowing the two water solutions into a container such as a laboratory flask or beaker, adding the second water solution to the first water solution, or adding the first water solution to the second water solution. Preferably, the resulting mixture of the first and second water solutions is stirred during this contacting step. Most preferably the first water solution (containing the silicate-containing salt) is

added with mixing to the second water solution (containing the silver-containing salt and all of the promoter-containing salts). The mixing of the first and second water solutions is carried out at room temperature and opened to the atmosphere.

A solid precipitates from the third water solution. The solid precipitate is filtered from its mother liquor.

5 The resulting filter cake is broken into smaller particles by conventional methods, such as by jabbing with a glass stirring rod. The particles are washed by suspending the particles in water, stirring, and then refiltering the suspended particles. The washing is repeated three times. The washed particles are dried, such as by drying in air at 150 °C overnight, to produce the catalyst.

When the two water solutions are contacted in the most preferred manner as described hereinabove, 10 the silver ions and promoter ions precipitate essentially simultaneously as a composition comprising a mixed silver-promoter silicate. As noted hereinbefore, the silicate is actually a distribution of silicate anions. The following theory is proposed to account for the improved activity of the mixed silver-promoter silicate catalyst; however, the scope of the invention should not be limited or bound to such a theory. It is believed that when the silver ions and promoter ions are precipitated simultaneously, the silver ions and promoter ions occupy nearest neighbor cation positions in the mixed silicate salts. In such a composition the silver ions and the promoter ions are in close proximity to each other. This composition contrasts with that in which a discrete silver silicate salt is physically mixed with a discrete promoter compound of any type, for example, in the case where the silver ions and promoter ions are deposited sequentially. It is believed that in such physical mixtures the nearest neighbor cation positions are occupied by ions of the same species, 15 that is, silver next to silver and promoter next to promoter, with some minor exception at the edges where the two salts contact. As will be seen in the Examples hereinafter, a catalyst prepared by the most preferred method of this invention and comprising the mixed silver-promoter silicate exhibits advantageous properties in the epoxidation of olefins.

20 The mixed silver-promoter silicate catalyst may be used as is, or may be used supported on an inert carrier. Any refractory oxide which does not interfere with the oxidation reaction will provide a suitable support. Examples of such suitable supports are alumina, silica, titania, alkaline earth oxides, rare earth oxides, and mixtures of the above. Alkaline earth carbonates also make suitable supports. Preferably, the support is a refractory oxide. More preferably, the support is silica. Most preferably, the support is Cab-O-Sil® M-5 fumed silica from Cabot Corporation.

25 The catalyst of this invention may be activated *in situ* in the olefin oxidation reaction, or optionally, activated prior to use. The activation comprises reducing the catalyst with an appropriate reducing agent. If the catalyst is activated *in situ*, the olefin itself, preferably propylene, is the reducing agent. If the catalyst is activated prior to use, the reduction is carried out by conventional methods, such as by heating overnight at 150 °C under one atmosphere of from 1 mole percent to 10 mole percent hydrogen in nitrogen. If desired, 30 more hydrogen --up to 100 mole percent-- may be used. By either method, the reduction produces silver metal and promoter metal in intimate contact with the mixed silver-promoter silicate salt. Typically, from 70 to 80 mole percent of the silver is reduced; whereas, the amount of reduced promoter depends on the reduction potential of the promoter and the reducing conditions. Typically, the promoter is not significantly reduced.

35 The activity of the catalyst of the invention may be tested in the epoxidation of propylene. To measure the performance, the following test can be constructed: The catalyst (10 g) is placed in a 3/8-inch (9.5 mm) inner diameter, stainless steel reactor, such that a reaction zone of 3 to 4 inches in length is created. Glass wool plugs are placed on either end of the reactor to retain the catalyst. A premixed feed is prepared consisting essentially of 70 volume percent propylene and 30 volume percent oxygen. The feed is passed 40 through a water saturator which saturates the feed with 3 volume percent water vapor. The water-saturated feed is preheated to the temperature of the reactor. The catalyst is then "burned in" by passing the premixed, preheated feed through the catalyst until the selectivity to propylene oxide stabilizes (typically 5 days). The "burn in" is conducted at a temperature in the range of from 150 °C to 180 °C, a pressure in the range of from 15 psia to 250 psia (0.1 to 1.7 MPa absolute), and a flow rate in the range of from 10 cc/min to 300 cc/min. The conversion of propylene, selectivity to propylene oxide and specific epoxidation rate are calculated from a gas phase chromatographic analysis of the product stream. Preferably, a catalyst of this invention produces simultaneously a conversion of propylene greater than 0.2 mole percent, a selectivity to propylene oxide greater than 28 mole percent, and a specific epoxidation rate of at least 0.8 gram of propylene oxide per kilogram of silver per hour.

45 50 55 The catalyst compositions of this invention typically have surface areas between 0.1 m²/g and 200 m²/g. Preferably the surface area of the catalyst is greater than 10 m²/g, more preferably greater than 50 m²/g, most preferably greater than 70 m²/g. Preferably the surface area of the catalyst is less than 180 m²/g, more preferably less than 150 m²/g, most preferably less than 120 m²/g.

The catalyst compositions of this invention may be used in the direct oxidation of olefins by oxygen to yield the corresponding olefin oxides. Such a process comprises contacting the olefin with oxygen in the presence of the catalyst composition, described hereinbefore, under conditions such that the olefin oxide is formed.

5 The olefins employed in the process of this invention are any higher olefins which are readily oxidized to epoxides in the presence of silver catalysts. A higher olefin is defined for the purposes of this invention as an olefin containing at least three carbon atoms. Examples of such olefins are propylene, 1-butene, 2-butene, 1-pentene, 2-pentene, styrene, and cyclohexene; however, the process is not limited solely to these examples. Preferably, the olefin is propylene. The olefin is preferably saturated with water vapor. This can be accomplished by bubbling the olefin through liquid water. Small amounts of a usual inhibitor, for example 0.001 to 5 ppm of 1,2-dichloroethane, may be used when the olefin is ethylene.

10 The oxygen employed in the process of this invention may be obtained from any gas containing molecular oxygen, such as air. The olefin and oxygen are present in an amount sufficient to allow formation of the epoxide of the olefin. Preferably, the oxygen to olefin mole ratio is above 0.01:1, more preferably above 0.05:1; the ratio is preferably below 2:1, more preferably below 0.40:1.

15 The reactants can be contacted with the catalyst in any suitable reactor. An example of a suitable reactor is the test reactor described hereinbefore. Preferred are tubular stainless steel reactors designed to withstand the pressure of the reaction. Typically plugs of glass wool are used to keep the catalyst in the reactor. While the contact of the olefin with oxygen and the catalyst can take place in either the vapor phase or in a liquid solvent, contact in the vapor phase is preferred. The feed is preferably preheated to a temperature about that of the reaction temperature.

20 The pressure and temperature should be adjusted to achieve optimal results for each catalyst and feed mixture. The pressure may be subatmospheric through superatmospheric with superatmospheric pressures preferred. It is more preferred to use a pressure of from 7 psia to 300 psia (0.05 to 2.1 MPa absolute). It is even more preferable to use a pressure of from 15 psia to 100 psia (0.1 to 0.7 MPa absolute).

25 The reaction can occur at any operable temperature upon contacting the catalyst and the reactants. Preferred is contact with a catalyst heated to a temperature above 50°C, more preferred is contact with a catalyst heated to a temperature above 100°C, and most preferred is contact with a catalyst heated to a temperature above 140°C. Preferred is contact with a catalyst heated to a temperature below 300°C, more preferred below 250°C, most preferred below 200°C.

30 The residence time of the reactants in the catalyst zone of the reactor is sufficient to allow for some epoxide formation. In general, the residence time will vary as a function of the scale of the reactor, the quantity of catalyst in the reactor, and the type of reactor. The residence time necessary to promote the desired epoxidation reaction is obtained by controlling the gas hourly space velocity of the reactants passing through the reaction zone. The gas hourly space velocity is expressed in units of volume of gas flow per hour per volume of reactor, or simply hr^{-1} , at a specified temperature and pressure. One can readily adjust the gas hourly space velocity to obtain the optimum reaction or contact time. For most reactors a space velocity in the range of from 10 hr^{-1} to 15,000 hr^{-1} measured at reaction conditions can be employed. Preferably, the space velocity is in the range of from 10 hr^{-1} to 6000 hr^{-1} . More preferably, the space velocity is in the range of from 50 hr^{-1} to 3000 hr^{-1} .

35 The reaction products are the epoxide of the olefin reactant, carbon dioxide, and water. The epoxides are useful intermediates, particularly useful in the manufacture of urethane polymers.

40 For the purposes of this invention, the term "conversion" is taken to mean the mole percent of olefin lost from the feed stream as a result of reaction. Likewise, the term "selectivity to olefin oxide" is taken to mean the mole percent of reacted olefin which goes to form olefin oxide. The conversion and selectivity of the process of this invention can vary over a wide range. Such process variables as the temperature, pressure, flow rate, concentration of oxygen, and concentration of water influence the conversion and selectivity. Generally, as the concentration of oxygen in the feed stream increases, the conversion of olefin also increases, while the selectivity for olefin oxide decreases. Generally, as the temperature of the reaction increases, the conversion also increases, while the selectivity decreases. By adjusting the process parameters of the invention, the skilled artisan can obtain simultaneously an acceptable conversion and a high selectivity in the epoxidation of the higher olefins, like propylene. Typically, the catalyst of this invention produces an olefin conversion of at least 0.1 percent. Preferably, the catalyst produces a conversion greater than 0.2 percent; more preferably a conversion greater than 0.6 percent; most preferably, greater than 1.0 percent. Typically, the catalyst of this invention produces a selectivity to olefin oxide greater than 20 percent. Preferably, the catalyst produces a selectivity to olefin oxide greater than 28 percent; more preferably, a selectivity greater than 40 percent; most preferably, greater than 50 percent.

45 In addition to the conversion and selectivity, a convenient measure of the activity of the mixed silver-

promoter silicate catalyst is the specific epoxidation rate. For the purposes of this invention, the term "specific epoxidation rate" is taken to mean the grams of olefin oxide formed per kilogram of silver per hour. Typically, the specific epoxidation rate is greater than 0.8 gram of olefin oxide formed per kilogram of silver per hour. Preferably, the specific epoxidation rate is greater than 3 grams of olefin oxide per kilogram of silver per hour; more preferably, greater than 6 grams of olefin oxide per kilogram of silver per hour.

5

The invention is further illustrated by the following, non-limiting examples. All percentages are given as mole percent, unless otherwise noted.

10 Example 1

A first solution was prepared containing $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (37.2 g, 131 mmoles) in 1.5 liters of water. A second solution was prepared containing AgNO_3 (36.4 g, 214 mmoles) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.3 g, 20.7 mmoles) in 1.5 liters of water. The first solution was added to the second solution at room temperature to form an orange precipitate. The resulting orange precipitate and mother liquor were heated at 95°C for one hour. The mixture was cooled to room temperature and filtered. The filter cake was washed by breaking up the cake and suspending the particles in 2.0 liters of water. The suspended particles were refiltered. The filter cake was washed two or three more times in the same manner. The washed filter cake was dried by heating at 150°C overnight. The dried cake was reduced at 125°C overnight with a 10 percent hydrogen in nitrogen gas mixture. The reduced material was used as an oxidation catalyst for propylene, as described hereinabove, to obtain the results shown in Table I.

25 Example 2

A solution containing predominately $\text{Si}_2\text{O}_5^{2-}$ was prepared by heating a solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (35.8 g, 126 mmoles) in 0.175 liter of water to boiling and then dropwise adding 7.6 ml of 16N HNO_3 , allowing any precipitate to dissolve before adding the next drop of HNO_3 . A second solution was prepared containing AgNO_3 (17.9 g, 106 mmoles) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.66 g, 10.4 mmoles) in 2.0 liters of water. The second solution was heated to 90°C. The $\text{Si}_2\text{O}_5^{2-}$ solution was added to the heated second solution at a rate of 50 ml/minute to form an orange-yellow precipitate. This precipitate was heated with the mother liquor at 90°C for 2 hours, then cooled to room temperature and filtered. The filtered solid was washed, dried, reduced at 100°C-200°C and used as a catalyst as in Example 1. The oxidation activity is shown in Table I.

35

Example 3

A solution containing predominately $\text{Si}_3\text{O}_7^{2-}$ was prepared by heating a solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (58.5 g, 206 mmoles) in 0.20 liter of water to boiling, and then adding 16 ml of 16N HNO_3 in the same manner as described in Example 2. This solution was diluted with water to a total volume of 1.20 liters. A second solution was prepared containing AgNO_3 (20.7 g, 122 mmoles) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3.04 g, 119 mmoles) in 2.0 liters of water. The second solution was heated to 90°C. The diluted $\text{Si}_3\text{O}_7^{2-}$ solution was added to the heated second solution at a rate of 50 ml/minute to form a yellow precipitate. This precipitate was heated with the mother liquor at 90°C for 2 hours, then cooled to room temperature and filtered. The filtered solid was washed, dried, reduced at 100°C-200°C and used as a catalyst as in Example 1, with the results given in Table I.

40 Example 4

Cab-O-Sil®, M-5 brand fumed silica (20.39 g) was suspended in 1.75 liters of water containing dissolved $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (8.81 g, 31 mmoles). The suspension was heated at 90°C for one hour. A second solution was prepared containing AgNO_3 (8.70 g, 51.2 mmoles) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.32 g, 5.2 mmoles) in 2.0 liters of water heated at 90°C. The Cab-O-Sil® suspension was added to the heated second solution to form a precipitate which was heated with the mother liquor at 95°C for 2 hours, then cooled to room temperature and filtered. The filtered solid was washed, dried, reduced at 150°C and used as described in Example 1. The results are given in Table I.

Example 5

5 Cab-O-Sil® M-5 brand fumed silica (21.35 g) was suspended in 1.5 liters of water. In a separate flask a solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (17.7 g, 62.3 mmoles) in 0.10 liter of water was heated to boiling and 4 ml of 16N HNO_3 was added as described in Example 2. The heated solution was added to the suspension forming an enriched suspension. A second solution was prepared containing AgNO_3 (8.77 g, 51.9 mmoles) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.35 g, 5.27 mmoles) in 2.0 liters of water. The enriched suspension was added to the second solution at 90 °C to produce an orange precipitate which was heated with the mother liquor at 90 °C for 90 minutes. Afterwards the precipitate was cooled to room temperature, filtered, washed, dried, reduced at 150 °C and used as described in Example 1. The results are found in Table I.

Example 6

15 A first solution was prepared by dissolving $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (51.68 g, 182 mmoles) in 200 ml of water, adding 11.4 ml of concentrated HNO_3 , and diluting with water to a total volume of 2.0 liters. A second solution of AgNO_3 (25.59 g, 151 mmoles) and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (4.73 g, 10.6 mmoles) in 2.0 liters of water was added to the first solution. A precipitate formed and was heated for two hours at 90 °C in the presence of the mother liquor. The precipitate was filtered, washed, dried, reduced and used as described in Example 1 with the results shown in Table I.

Example 7

25 A first solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (38.7 g, 136 mmoles) in 1.60 liters of water was added to a second solution of AgNO_3 (36.7 g, 216 mmoles) and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (5.01 g, 21.2 mmoles) in 1.50 liters of water. The resulting precipitate was washed, dried, reduced and used as described in Example 1 with results shown in Table I.

Example 8

30 A first solution was prepared by dissolving $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (51.66 g, 182 mmoles) in 200 ml of water, heating to boiling, adding 11.5 cc of concentrated HNO_3 , and diluting with water to a total volume of 2.0 liters. A second solution was prepared containing AgNO_3 (25.51 g, 150 mmoles) and $\text{Lu}(\text{NO}_3)_3 \cdot 17.4\%$ percent H_2O (4.41 g, 8.43 mmoles) in 2.0 liters of water. The first solution was added to the second solution, and the resulting precipitate was heated at 90 °C for two hours. The precipitate was washed, dried, reduced and used as described in Example 1 with results shown in Table I.

Example 9

40 A first solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (37.1 g, 131 mmoles) in 1.5 liters of water was added to a second solution of AgNO_3 (36.1 g, 213 mmoles) and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (6.55 g, 21.2 mmoles) in 1.5 liters of water. The resulting precipitate was washed, dried, reduced and used as described in Example 1 with results shown in Table I.

Example 10

50 A first solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (38.2 g, 134 mmoles) in 1.5 liters of water was added to a second solution of AgNO_3 (36.6 g, 216 mmoles) and $\text{Cu}(\text{NO}_3)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ (5.03 g, 21.6 mmoles) in 1.5 liters of water. The resulting precipitate was washed, dried, reduced and used as described in Example 1 with results shown in Table I.

Example 11

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A first solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (38.9 g, 137 mmoles) in 1.5 liters of water was added to a second solution of AgNO_3 (36.3 g, 214 mmoles) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (6.46 g, 22.2 mmoles) in 1.5 liters of water. The resulting precipitate was washed, dried, reduced and used as described in Example 1 with results shown in Table I.

5

Example 12

A first solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (38.9 g, 137 mmoles) in 1.5 liters of water was added to a second solution of AgNO_3 (36.5 g, 215 mmoles) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (6.25 g, 21.5 mmoles) in 1.5 liters of water. The resulting precipitate was washed, dried, reduced and used as described in Example 1 with results shown in Table I.

15 Example 13

A first solution was prepared by dissolving $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (52.24 g, 184 mmoles) in 200 ml of water, heating to boiling, adding slowly 11.5 cc of concentrated HNO_3 , and diluting with water to a total volume of 2.0 liters. A second solution was prepared by dissolving AgNO_3 (25.68 g, 151 mmoles) and $\text{Pr}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (4.43 g, 13 mmoles) in 2.0 liters of water at 90 °C. The first solution was added to the second solution, and the resulting precipitate and mother liquor were heated at 90 °C for two hours. The resulting precipitate was washed, dried, reduced at 150 °C, and used as described in Example 1 with results shown in Table I.

25 Example 14

A first solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (39.8 g, 141 mmoles) in 1.5 liters of water was added to a second solution of AgNO_3 (36.3 g, 214 mmoles), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2.51 g, 10.9 mmoles), and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3.19 g, 10.7 mmoles) in 1.5 liters of water. The resulting precipitate was washed, dried, reduced and used as described in Example 1 with results shown in Table I.

Example 15

35 A first solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (40.0 g, 141 mmoles) in 1.5 liters of water was added to a second solution of AgNO_3 (37.4 g, 221 mmoles), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2.58 g, 10.9 mmoles), and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (3.36 g, 10.9 mmoles) in 1.5 liters of water. The resulting precipitate was washed, dried, reduced and used as described in Example 1 with results shown in Table I.

40 Example 16

A first solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (56.5 g, 199 mmoles) in 1.2 liters of water at 90 °C was added to a second solution at 90 °C, prepared as follows: A solution of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (4.51 g, 9.30 mmoles) in 5 ml of 16N HNO_3 was diluted with several ml of water. AgNO_3 (39.9 g, 235 mmoles) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.99 g, 23.4 mmoles) were added to the diluted $\text{Bi}(\text{NO}_3)_3$ solution, the resulting mixture was further diluted with water to 1.5 liters volume. The resulting precipitate was heated with the mother liquor for 2 hours at 90 °C; then cooled, washed, dried, reduced and used as described in Example 1 with the results shown in Table I.

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Oxidation of Propylene*						
Example No.	Catalyst wt (g)	Temp (°C)	Flow, cc/min	% Conversion	% Selectivity	SER*
5	1	180	10	12.3	16.8	2.6
		140	10	1.74	49.7	1.1
		121	10	0.40	57.0	2.8
		138	10	1.35	54.6	0.92
		180	50	3.73	47.2	16.0
10	2	150	50	0.85	60.8	4.7
		120	20	0.27	63.2	0.62
		155	50	1.13	60.2	6.2
		165	50	3.63	42.9	13.9
15	3	145	50	1.33	53.9	6.4
		115	20	0.46	57.4	0.95
		140	50	1.07	55.6	5.3
20	4	180	20	2.84	25.6	7.95
		150	10	0.88	37.6	1.8
		135	10	0.40	39.7	0.87
		190	60	2.38	33.7	34.8
25	5	160	60	0.40	54.6	9.5
		190	150	0.95	41.4	42.7
30	6	150	100	0.40	59.6	5.22
		170	100	1.49	50.6	16.6
35	7	165	10	1.15	33.3	0.93
	8	120	100	0.54	31.5	4.0
	9	150	10	1.32	38.0	1.2
	10	140	10	0.83	36.6	0.73
	11	150	10	1.45	39.2	1.37
	12	150	10	1.78	28.4	1.22
40	13	150	100	0.33	58.4	4.2
		170	100	1.01	54.5	12.0
45	14	145	20	1.25	44.3	2.7
	15	135	10	1.28	47.1	1.5
	16	130	10	1.41	50.4	1.7

* Feedstream: 70% (vol) propylene and 30% (vol) oxygen premixed, then saturated with H₂O at 25 °C to 3% (vol) H₂O vapor. Pressure, 14.6 psia (0.1 MPa absolute). SER = g propylene oxide kg⁻¹ Ag hr⁻¹.

45 The data in Table I show the activity of the catalysts prepared in Examples 1-16 in the oxidation of propylene. It is seen that the process conditions for the oxidation reaction are quite mild. A wide range of conversions is observed from a low of 0.4 mole percent to a high of 12.3 mole percent. Generally, the selectivity to propylene oxide is observed to be high. The lowest of such observed selectivities is 16.8 mole percent, while the highest was 63.2 mole percent. The selective epoxidation rate was found to be surprisingly good, ranging from a low of 0.62 g propylene oxide per kg silver per hour to a high of 42.7 g propylene oxide per kg silver per hour.

55 Example 17

A first solution comprising Si₂O₅⁻² was prepared by adding 19.0 ml of concentrated (16 M) nitric acid with stirring to a solution of NaSiO₃ · 9H₂O (91.30 g; 350 mmoles) in 200 ml of boiling water. In a separate flask Cab-O-Sil® M-5 Fumed Silica (106.38 g; Cabot Corp.) was suspended in 2.0 liters of water at 90 °C.

The $\text{Si}_2\text{O}_5^{2-}$ solution was added to the suspension of Fumed Silica, and the resulting $\text{Si}_2\text{O}_5^{2-}$ /Fumed Silica mixture was heated at 90°C with stirring. AgNO_3 (42.04 g; 250 mmoles) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (9.52 g; 37 mmoles) were heated with stirring in 2.0 liters of water at 90°C to make a second solution. The $\text{Si}_2\text{O}_5^{2-}$ /Fumed Silica mixture was then added to the second solution at the rate of 60 cc/minute. The resulting mixture was heated at 90°C for 2 hours. The mixture was cooled overnight. The precipitate was filtered; and then resuspended in 2.0 liters of water and refiltered. The resuspension and refiltration were repeated three times. The resulting filtercake was dried in air overnight at 150°C. The dried filtercake was reduced in 5 percent hydrogen in nitrogen; the reduction commencing at room temperature and continuing at a rate of 5°C/minute to 200°C, where the reduction was maintained for two hours. The solid was cooled to room temperature under the hydrogen and nitrogen stream to yield a mixed silver-magnesium silicate catalyst. The catalyst was used in the epoxidation of propylene with the results given in Table II.

TABLE II*

<u>Ex. 17</u>	<u>Pressure, psia (MPa Absolute)</u>	<u>Temp (°C)</u>	<u>Flow (cc/min)</u>	<u>% O₂ (vol)</u>	<u>% H₂O (vol)</u>	<u>% Con- version</u>	<u>% Selec- tivity</u>	<u>SER</u>
(a)	14.6 (0.1)	130	70	25.6	3	0.27	48.8	6.0
(b)	14.6 (0.1)	140	60	10.5	3	0.11	59.9	3.2
(c)	14.6 (0.1)	140	70	25.2	3	0.53	44.7	10.8
(d)	14.6 (0.1)	160	70	13.4	3	1.16	22.2	13.8
(e)	53 (0.35)	170	2000	23.4	0.1	0.26	54.3	26.5
(f)	53 (0.35)	170	2000	22.7	0.5	0.26	63.8	31.1
(g)	53 (0.35)	170	720	22.3	0.1	0.38	68.1	48.6
(h)	63 (0.4)	170	720	21.9 (37°C)	0.3 0.42	72.6	58.6	
(i)	75 (0.4)	170	1100	10.9	0.1	0.39	73.8	97.4
(j)	75 (0.4)	185	1100	11.0	0.1	0.24	51.0	41.8

* Feed: Propylene and oxygen were premixed in the indicated volume %, then bubbled through H_2O at 25°C, unless noted otherwise, to the indicated % (vol) H_2O vapor.

Catalyst: a-d, 10.0g; e-i, 25.0g. SER = g propylene oxide per kg Ag per hour.

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The data in Table II indicate the trends and ranges in conversion, selectivity, and selective epoxidation rate which were obtained on varying the process parameters. For example, it is seen that as the pressure increased (17g vs. 17h), the conversion of propylene and selectivity for propylene oxide increased. The conversion of propylene is seen to range from a low of 0.11 mole percent to a high of 1.16 mole percent.

5 The selectivity to propylene oxide is seen to range from a low of 22.2 mole percent to a high of 73.8 mole percent. The selective epoxidation rate is seen to range from a low of 3.2 g propylene oxide per kg Ag per hr to a high of 97.4 g propylene oxide per kg Ag per hr.

10 Example 18

A catalyst was prepared as described in Example 2. The catalyst was used in the epoxidation of propylene with the results shown in Table III.

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TABLE III*

20	Ex. 18	% O ₂ (vol)	% H ₂ O (vol)	T H ₂ O Bath, (°C)	% Conversion	% Selectivity	SER
	(a)	33	3.1	25	0.88	52.0	6.8
25	(b)	33	5.5	35	1.83	47.0	12.9
	(c)	33	9.3	45	2.25	36.6	12.3
30	(d)	19	0.6	0	0.27	52.3	2.6
	(e)	19	4.2	30	0.33	55.1	3.3
	(f)	19	7.30	40	0.42	50.2	3.8
	(g)	19	12.2	50	0.66	42.2	5.0

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* Feed: Propylene and oxygen were premixed in the indicated % (vol), then bubbled through water at 25°C to the indicated % (vol) water vapor. Catalyst: 25.0g; Pressure: 14.6 psia (0.1 MPa absolute); T: 155°C; Flow rate: 50 cc/min. SER = g propylene oxide per kg Ag per hour.

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The data in Table III indicate the trends and ranges in conversion, selectivity, and selective epoxidation rate which were obtained on varying the oxygen and water concentrations. As the concentration of water increased (18a-c, d-g), the conversion increased, while the selectivity for propylene oxide typically decreased. As the concentration of oxygen increased (18a vs 18e), the conversion increased. The conversion of propylene is seen to range from a low of 0.27 mole percent to a high of 2.25 mole percent. The selectivity to propylene oxide is seen to range from a low of 36.6 mole percent to a high of 55.1 mole percent. The selective epoxidation rate is seen to range from a low of 2.6 g propylene oxide per kg Ag per hr to a high of 12.9 g propylene oxide per kg Ag per hr.

55 **Claims**

1. A process of epoxidizing higher olefins comprising contacting at least one higher olefin with oxygen in the presence of a catalyst, characterised in that a catalyst is used which is prepared by contacting in an aqueous solution the following dissolved salts:

5 (a) a silver-containing salt;
(b) at least one salt containing a multivalent cation promoter; and
(c) a silicon-containing salt, wherein the mole ratio of silicon to combined silver and promoter metals is at least 0.5,

thereby forming a mixed silver-promoter silicate precipitate which when tested as a catalyst in the epoxidation of propylene produces a conversion of propylene greater than 0.2 mole percent and a selectivity to propylene oxide greater than 28 mole percent.

10 2. A process as claimed in Claim 1 wherein the mole ration of silver to combined promoter metals is greater than 1.4:1 and less than 100:1.

3. A process as claimed in Claim 1 in which the silver salt is silver nitrate; the silicate salt is sodium silicate and the higher olefin is propylene.

15 4. A process as claimed in Claim 1 in which the promoter salt is a water-soluble nitrate having a dipositive or tripositive cation selected from beryllium, magnesium, calcium, strontium, barium, cobalt, nickel, copper, zinc, cadmium, praseodymium, neodymium, europium, gadolinium, holmium and lutetium or mixtures thereof.

20 5. A process as claimed in Claim 1 wherein the oxygen to olefin mole ratio is above 0.05:1 and below 0.40:1; the temperature is above 100 °C and below 250 °C; the pressure is in the range of from 7 psia to 300 psia (0.05 to 2.1 MPa absolute); and the space velocity is in the range of from 10 hr⁻¹ to 6000 hr⁻¹.

6. A process as claimed in Claim 1 wherein (1) the conversion of olefin is greater than 0.6 mole percent and the selectivity to olefin oxide is greater than 40 mole percent or (2) the conversion of olefin is greater than 1.0 mole percent and the selectivity to olefin oxide is greater than 50 mole percent.

25 7. A process as claimed in Claim 1 wherein the specific epoxidation rate is (1) greater than 0.8 gram of olefin oxide formed per kilogram of silver per hour or (2) greater than 3 grams of olefin oxide formed per kilogram of silver per hour.

8. A process as claimed in Claim 1 wherein the catalyst is supported on fumed silica.

9. A process for preparing a catalyst characterized by contacting in an aqueous solution the following dissolved salts:

30 (a) a silver-containing salt;
(b) at least one salt containing a multivalent cation promoter; and
(c) a silicon-containing salt, wherein the mole ratio of silicon to combined silver and promoter metals is at least 0.5,

35 thereby forming a mixed silver-promoter silicate precipitate.

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